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Applicant: Kojundo Chemical Laboratory Co., Ltd.

Specification

1. Title of the Invention

METHOD OF MANUFACTURING AN OXIDE FILM OF SEMICONDUCTOR DEVICE

2. Scope of Patent claims

(1) A method of manufacturing an oxide film of a semiconductor device, characterized in that components of a plasma gas except for a raw material gas are nitrogen within a range of from 50 to 100%, and are other gases in a range of from 0 to 50%, in a plasma CVD method for growing the raw material gas in a chemical vapor phase by using plasma.

(2) A method of manufacturing an oxide film according to claim 1, wherein the other gas is one selected from the group consisting of hydrogen, oxygen, helium, neon, ammonia and hydrazine, or a mixture of two kinds or more of these substances.

3. Detailed Description of the Invention

(Object of the Invention)

Field of the Industrial Application

The present invention relates to a method of manufacturing an oxide film of a semiconductor device for forming a film by using a plasma CVD method.

Prior Art

The plasma CVD method is a method for forming a thin film by generating plasma by high frequency excitation under a pressure from 0.1 to 100 Torr. A raw material gas is changed to radicals of atoms and molecules of high activity within the plasma of glow discharge, and reactivity of these radicals is utilized. Accordingly, a reaction can be caused at a low temperature equal to or lower than 400°C.

The plasma CVD method was first practically used to form a silicon (Si) nitride film having an excellent property as a passivation film.

The plasma CVD method of an oxide film lies at a developing stage at present.

When an SiO_2 film is formed on a substrate by the plasma CVD method, tetraethoxysilane [$Si(OC_2H_5)_4$] gas is used as a raw material and a mixing gas of this gas and oxygen is used in a general technique. However, in this mixing gas, there is

a defect in that an alkyl group such as a CH_3 group and a CH_2 CH_3 group is left within the SiO_2 film so that film characteristics are inferior. To exclude this defect, a method using helium as the mixing gas instead of oxygen is proposed. However, no alkyl group can be sufficiently removed from the interior of the film even when this method is used. Thus, there is a defect in that the film characteristics are not necessarily improved.

Problems to be solved by the Invention

The present invention provides a method for manufacturing an oxide film of very good quality in which a CH_3 group and a CH_2 CH_3 group are not left within this film when alcoholate including silicon such as tetraethoxysilane is set to a raw material and the oxide film is formed on a substrate by using the plasma CVD method.

(Construction of the Invention)

Means for solving the Problems

The present invention is characterized in that an oxide film is formed on a substrate by the plasma CVD method using a raw material gas such as tetraethoxysilane and nitrogen, or a mixing gas of nitrogen and other gases.

In accordance with this method, no alkyl group is left within the oxide film so that the oxide film of very good quality can be manufactured.

A gas selected from the group consisting of Hydrogen, oxygen, helium, neon, ammonia and hydrazine, or a mixture gas of two kinds or more of these substances can be used in the other gases mixed with nitrogen.

In the present invention, when only nitrogen is used in the mixing gas with the raw material gas, no OH group is easily left in the oxide film so that adhesive strength of the substrate and the oxide film is insufficient in a certain case. In this case, this adhesive force can be adjusted by slightly mixing hydrogen.

In the present invention, nitrogen is used as a plasma gas. However, no nitrogen compound is formed within the oxide film to such an extent that etching of the oxide film is obstructed by the nitrogen compound.

The present invention can be also applied to the formation of a transparent electrode film such as ITO (In_2O_3 + SnO_2), or a dielectric film such as Ta_2O_5 in addition to an insulating film such as SiO_2.

Further, in the conventional manufacturing method of the oxide film using the plasma CVD method, tetramethoxysilane [$Si(OCH_3)_4$] as a raw material gas cannot almost used since a large amount of alkyl group is left within the oxide film. However, in the present invention, no alkyl group is left in the oxide film. Therefore, similar to tetraethoxysilane,

tetramethoxysilane can be used as the raw material gas of the oxide film.

Example

A silicon (Si) substrate is arranged within a plasma CVD device, and is heated to 100°C.

On the other hand, nitrogen of 10 cc/min is bubbled within a container storing tetraethoxysilane at 25°C, and a gas of tetraethoxysilane is introduced into the plasma CVD device together with nitrogen. The pressure within the device is 2 Torr. A plasma CVD film is formed on the substrate at high frequency of power 70 W.

An infrared absorption spectrum of the formed oxide film is measured. As a result, no absorption spectrums of an alkyl group and an OH group are observed.

When plasma is generated in the same condition, nitrogen plasma is very bright in comparison with oxygen plasma. Accordingly, it has been found that plasma temperature is very high.

(Effect of the Invention)

Accordance to the present invention, no alkyl group such as the CH_3 group or the CH_2 CH_3 group is left within the formed oxide film. Therefore, the present invention is characterized in that quality of the oxide film is very preferable.

In comparison with the oxygen plasma, the nitrogen plasma

has large plasma energy, and the speed of a chemical reaction through the plasma is increased. Therefore, a forming speed of the oxide film is increased so that a manufacturing time of the oxide film is shortened.

Further, there is an advantage in that a usage of the raw material gas is small so that manufacturing cost is reduced.

Further, an electric field and charged particles of high energy are concerned in the plasma CVD so that the substrate and a deposited film are easily damaged. In a submicron pattern, there is a fear that this damage has an adverse effect on a device. However, the present invention is characterized in that this damage due to sputtering is small since the molecular weight of nitrogen is smaller than that of oxygen.

In the conventional plasma CVD method using oxygen, there is a defect in that an intermediate polymerization substance of a tar shape is easily collected in the pump of a vacuum exhaust system within the plasma CVD device. However, in the present invention, this intermediate polymerization substance is not easily collected in the pump so that the plasma CVD device is easily maintained.

Further, there are defects in that helium as a plasma gas is expensive and that oxygen easily damages an electrode, a probe and the like within the plasma CVD device. However,

there is an advantage in that nitrogen is cheap and easily treated.